

ASSESSMENT OF ATMOSPHERIC DEPOSITION EFFECTS ON NATIONAL FORESTS

Protocols for Collection of Supplemental Stream Water and Soil Composition Data for the MAGIC Model

June 2004

Prepared For:

USDA Forest Service 160 Zillicoa Street, Suite A, Asheville, NC 28801

Prepared by:

J.R. Webb, University of Virginia
T.J. Sullivan, E&S Environmental Chemistry, Inc.
B. Jackson, USDA Forest Service

E&S Report 03-05-01

E&S Environmental Chemistry, Inc.
P.O. Box 609 Corvallis, OR 97339

CONTENTS

1.0	PURPOSE	3
2.0	THE NEED FOR SUPPLEMENTAL DATA	3
3.0	STREAM WATER DATA COLLECTION	5
4.0	SOIL DATA COLLECTION	20
5.0	SAFETY ISSUES	28
6.0	CITATIONS	29
Appendix A: Listing of Protocols and Methods Manuals Reviewed		31
Appendix B: Forest Service Data Collection Forms and Instructions		32
Appendix C: A Summary Listing of Instrumentation and Techniques Employed by the University of Virginia		41
Appendix D: Field Data Forms for the Soil Sampling Components of the Assessment Project		44

1.0 PURPOSE

Numerous National Forests of the USDA Forest Service have initiated assessments to determine if acidic deposition is adversely affecting the health of forested watersheds. The focus of this document is to describe the water and soil sampling protocols for the Cherokee, Pisgah, Nantahala, and Sumter National Forests. An important Forest Service (FS) goal is to identify which watersheds may be experiencing, or are predicted to experience, base-cation depletion. The principal surrogate used to indicate watershed acid-base status and associated soil base saturation is stream water acid-neutralizing capacity (ANC). Stream water data, including ANC, have been obtained from a number of watersheds. Additional work will involve application of MAGIC (Model of Acidification of Groundwater in Catchments; Cosby et al. 1985a,b) to predict future watershed conditions and determine critical loads of future atmospheric deposition that may be required to provide adequate resource protection. Watersheds that currently have, or are predicted in the future to have, stream water ANC below a critical threshold may be candidates for more-intensive study and perhaps intervention with specific fertilization to improve watershed health. This protocol document is designed to support additional water quality and soils data collection that may be needed in association with this modeling and assessment effort. The purpose of this protocol is primarily to provide data for MAGIC modeling, but the resulting data could also be used in more general assessment efforts aimed at understanding acidification and nutrient depletion cause/effect relationships within the study areas.

The general provisions of this protocol were derived from a number of protocol documents associated with acidic deposition effects assessments and other studies of upland watersheds (Appendix A provides a listing of protocols and methods manuals reviewed). The specific provisions of this protocol have been determined by the need for efficiency and the specific data input requirements of the MAGIC model.

2.0 THE NEED FOR SUPPLEMENTAL DATA

Although the FS seeks to assess previous, current and future forest health effects of acidic deposition, water quality and especially soils data are available for only a subset of the watersheds that are potentially of concern. Decisions to collect additional data will need to address the adequacy of existing data as a basis for characterizing current acid-base status (stream water ANC and soil base cation supply) and to reliably model the future acid-base status of the population of acid-sensitive watersheds within the region.

2.1 Water Quality Data

The adequacy of available water quality data can be determined based on the distribution of sampled sites across geologic sensitivity classes (where there have been no previous glaciations), capacity to regionalize information on current status, and on the need for additional data for MAGIC model application. In the absence of probability-based site selection, effective regionalization will depend on the ability to explain variance in the available data as a function of mappable landscape characteristics.

Previous work in the southern Appalachian region has shown the acid-base status of surface waters (and watershed soils) is mainly a function of watershed bedrock type (c.f., Sullivan et al. 2002). Within the model, the importance of bedrock type is reflected in the soils acid-base chemistry data that are associated with a given bedrock type and the drainage water chemistry data that reflect spatial and temporal integration of lithologic and edaphic factors within the watershed. The availability of regional-scale geologic maps thus provides a basis for regionalization of water quality data obtained for a limited number of sites. Statistical analyses can be used to determine the relationship between the available water quality data and defined bedrock classes present in the subject watersheds. Decisions to collect more water quality data or to simply rely on available data should be based, in part, on the strength of the observed relationships and the degree of coverage with respect to the range of bedrock classes in the region. Additional decisions to collect more water quality data may relate to the input needs of MAGIC and to decisions concerning co-location of water quality and soils data collection.

Selection of sites for additional water quality sampling should be based on systematic and documented criteria. The criteria should include representation of bedrock and/or soil classes, geographic distribution, elevation, watershed size, site accessibility, and avoidance of watersheds with disturbance that might influence stream water composition. Approximate sampling site locations can be identified on a preliminary basis prior to initial sampling trips, with specific site selection and further documentation developed in association with sampling, as described below.

Additional decisions will need to be made concerning the frequency of sampling. Springtime samples are usually regarded as the best representation of water quality when only single samples can be collected. Better representation of annual conditions can be obtained with seasonal or other periodic sampling.

2.2 Soil Composition Data

There is very little soil acid-base chemistry data available for FS lands (especially in the North Carolina, South Carolina, or Tennessee) that are adequate for calibrating the MAGIC model. Initial MAGIC model calibration to a particular stream might therefore depend on the use of soils data from similar landscapes (for example, with similar or closely-related geologies) in the surrounding region. Collection and analysis of soils samples within each of the watersheds (or catchments) to be modeled is the preferred approach. However, if that is not possible, regional-scale geologic maps and defined bedrock classes could provide a basis for assigning available soils data to each of the specific watersheds to be modeled (Caution will need to be used since some area may have a geological outcrop that results in a subtle chemistry changes in the catchments). The adequacy of this approach can be evaluated based on the level of uncertainty (or range of possible ANC values) for model output associated with individual watersheds or groups of watersheds defined by bedrock class. In general, we recommend collection of soils within each watershed to be modeled. Additional soils data will certainly need to be collected if the uncertainty of model output is considered unacceptable or if soils data are not available to adequately represent the range of bedrock classes and soils types on those bedrock classes within the region.

Selection of watersheds, and sites within watersheds, for additional soils sampling should be based on systematic and documented criteria. The criteria should include such factors as representation of bedrock classes, topographic and geographic distributions, watershed size, site accessibility, and avoidance of watersheds with disturbance that might influence soil

composition. One approach to selecting specific sites in individual watersheds is to locate samples on midslope positions (in the catchment), with each selected to represent a contiguous unit of single bedrock type, forest cover, and slope class. The preferred approach is to collect samples from a limited number of soils sites (generally two or three soil pits per watershed for MAGIC calibration) that will be selected using a stratification process according to bedrock type, general soils type, and/or vegetation coverage. Resource and sampling logistical considerations may make it necessary to locate multiple sites in a small number of catchments rather than to distribute single sites among a larger number of larger (e.g., 6th level HUC) watersheds. Approximate sampling site locations can be identified on a preliminary basis prior to initial sampling trips, with specific site selection and documentation provided during sampling, as described below.

2.3 How the Data Might Be Used

The resulting soils and water quality data can be used to calibrate the MAGIC model to one or more specific watersheds, each defined as the area of land that drains to a particular stream sampling point. Model calibrations can then form the basis for estimating past acidification and/or projecting future changes in stream water chemistry on a site-specific (c.f., Sullivan et al. 2003) or regional (c.f., Sullivan et al. 2002) basis. The model output data could also be used to estimate the critical load of deposition that would be required to protect water acid-base chemistry against acidification to specified critical levels, such as ANC = 0, 20, or 50 $\mu\text{eq/L}$ (c.f., Sullivan and Cosby 2002, Sullivan et al. 2003).

3.0 STREAM WATER DATA COLLECTION

3.1 Arrangements with the Water Chemistry Laboratory

Appropriate agreements or contracts will need to be made with a qualified water chemistry laboratory well in advance of field sampling. Besides processing the water samples, the laboratory should prepare and provide sample bottles, insulated shipping containers, and refrigerant, as described below (sections 3.2.3 and 3.2.4). Historically, the USFS/USGS Water and Soil Lab in Fort Collins, Colorado has performed the analyses on water chemistry samples collected in the National Forests of western North Carolina, eastern Tennessee and the upstate of South Carolina.

3.2 Sampling Materials

Each person or sample-collection team should be provided the following equipment and materials, except as noted.

More details on equipment and materials follow in sections 3.2.1–3.2.4. Instructions for use are in sections 3.3 and 3.4.

- Site information folders (including maps and Stream Water Field Data Forms)
- Site documentation materials
- Sampling protocol (this document)
- Sampling bottles (each preferably placed in a plastic bag)
- Plastic gloves stored in a secure plastic bag
- Insulated containers, refrigerant, and backpacks
- Thermometer
- Wrist watch
- Survey grade global positioning system and compass
- 50 or 100 meter tape (and, if available, laser rangefinder) to measure distances
- Labels and waterproof markers
- Number 2 pencils, or write-in-rain pens, and notebooks
- Digital camera with extra memory cards and battery
- Aluminum tags if the sites are being established for long-term monitoring of water chemistry

3.2.1 Site Information Folders

The water chemistry samples taken on National Forest lands in North Carolina, South Carolina and Tennessee are collected within a Wilderness, or 6th level Hydrologic Unit Code (HUC) to determine if any of the area of interest may have low amounts of bases to neutralize the acids from natural and anthropogenic sources. The 6th level HUC was chosen because the Forest Service may own a large percentage (20 percent or more) of these watersheds. Typically, 10 first or second order streams are chosen in each HUC to be sampled. The criteria taken into consideration for the stream selections include ease of accessing the site, lithology, wet sulfate deposition estimates, elevation, and if the area has special significance (for example, a wilderness). The information documenting the site information, the sample information, and field measurements (see the field data sheet in Appendix B) for each sample site will be found in the HUC folder.

Site documentation information in the site folders will include site maps, narrative access descriptions, site coordinates and elevation, site-tag numbers (for long-term monitoring sites) and locations, and site photographs.

Maps will include 1:24,000 USGS quadrangle maps with sampling sites identified and Forest recreation maps to help navigate to the area. Maps generated using GIS will also be included to show where the project manager has selected potential sites to sample (see Figure 1 below), or where the sites were sampled in a previous survey.

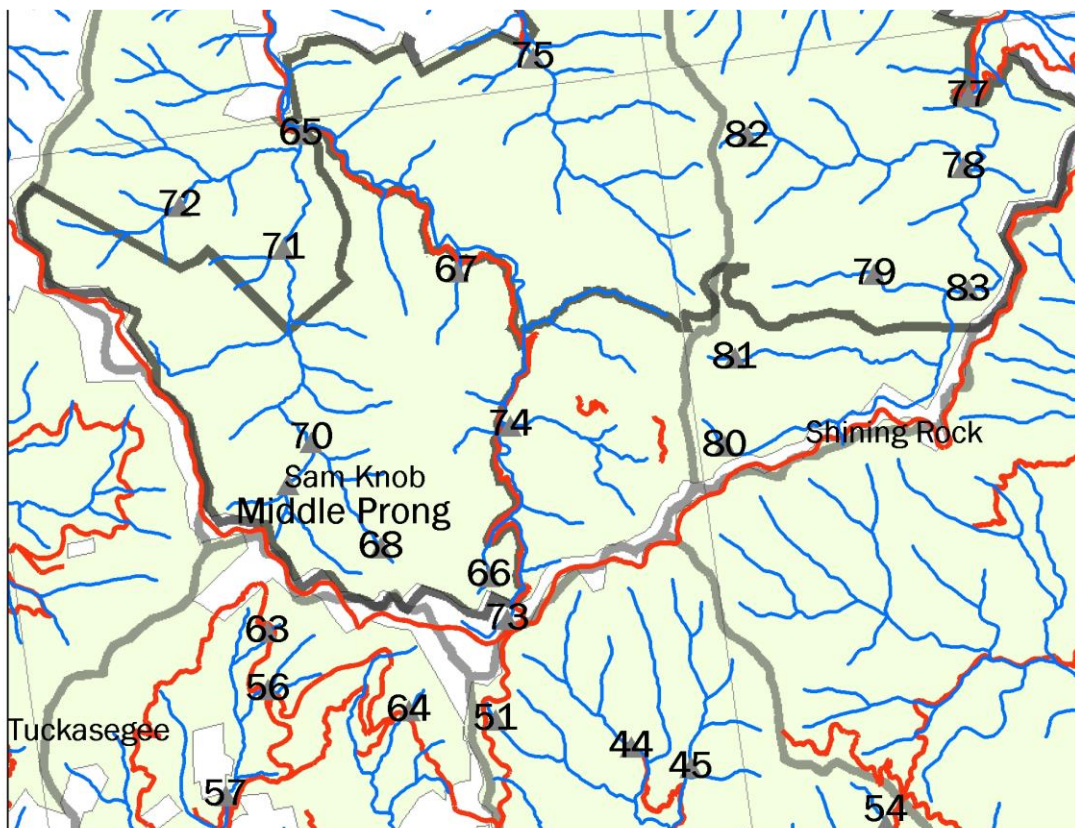


Figure 1. Example of a GIS-generated preliminary sampling site map. The site numbers and triangular symbols indicate preliminary or approximate sampling site locations. Selection of the specific sampling site is based on conditions observed in the field. USGS 1:24,000 quadrangle maps can also be used.

The Surface Water Chemistry Long-Term Monitoring Record data sheets will serve for documenting site information, sample locations and field measurements. These forms should be printed on waterproof paper if rainy weather is expected during the field sampling. A copy of the Surface Water Chemistry Long-Term Monitoring Record data sheet is provided in Appendix B.

3.2.2 Site Documentation Materials

In addition to the material described above for inclusion in site documentation folders, site documentation materials should also include uniquely numbered aluminum tags for sites planned to be sampled repeatedly (i.e. monitoring sites) or replacement of missing tags at previously established sites, nails and a small hammer for tag placement, flagging tape, a camera for site photographs, a GPS unit for determination of geographic coordinates (in decimal

degrees). Waterproof pens and pencils (needed in wet conditions) should be provided for completing forms.

3.2.3 Sample Collection Bottles

As indicated previously, the lab that is performing the analysis should normally be responsible for bottle processing and packaging. Sample collection bottles should be 250 ml (large enough to allow reanalysis, if necessary), wide-mouth HDPE or LDPE Nalgene bottles. Bottle processing should involve multiple rinses with distilled water (see section 3.5). The processed bottles should be stored filled with deionized water, which will be poured out at the time of sample collection. Label tape should be affixed to the bottles prior to packaging.

The field crew will have to take extra precautions to ensure that no bottle mouth is contaminated with leaking refrigerant, tap water, dirt, or other foreign substance. Each processed bottle should be packaged individually in a zipper-lock type plastic bag if the laboratory analysis indicates that contamination is an issue.

3.2.4 Insulated Containers, Refrigerant, and Backpacks

As indicated previously, the lab performing the analysis should be responsible for provision of insulated containers and refrigerant. Field crews will also need backpacks with waterproof covers for transport of samples and other materials when hiking into sites that cannot be accessed by vehicle.

Insulated containers, with chemical refrigerant (“blue-ice”), are needed for transport of collected samples between the field and the lab or other staging location. Small insulated containers that will fit into backpacks can be used to carry and protect the samples in the field. Larger insulated containers can be used for assembly and transport of samples in vehicles.

Ideally, chemical refrigerant packages should be packaged in zipper-lock type plastic bags to minimize the possibility of sample bottle contamination through leakage. The field crews will need to make sure the chemical refrigerant is placed in a freezer two days before sampling.

3.3 Sample Site Location and Documentation

Depending on the objectives for the field data collection, the field crews may be collecting water samples as part of a synoptic survey (inventory), or they may be repeating sampling at the same locations in a monitoring effort to examine changes in water chemistry over a period of time. The extent of documentation required will depend on whether the site is to be sampled once, or numerous times.

3.3.1 Locating Established Sampling Sites

Previously established sample-collection sites can be located by reference to maps provided in the HUC information folder, by reference to access notes provided on the Surface Water Chemistry Long-Term Monitoring Record data sheet, by reference to site photos, and by use of a GPS unit to determine geographic coordinates. It is desirable to enter site coordinates

into the GPS unit in advance of sampling trips. For sites with aluminum tree tags, site confirmation is provided by location of the tag.

Forest recreation maps provide orientation and general access information. Specific site location information will be provided by USGS 1:24,000 quadrangle maps with sites indicated. In some cases, multiple maps will be required to provide needed access information.

The Surface Water Chemistry Long-Term Monitoring Record data sheet provides access notes, describing the route to the site and the location of the site. In most cases, the sampling sites will be described as adjacent to, immediately above, or a specified distance and compass heading above or below a particular landmark. Landmarks include bridges, trail crossings, marked boundary lines, confluence points, and other identifiable fixed features. If existing access notes are insufficient, additional notes or clarification should be added to the Surface Water Chemistry Long-Term Monitoring Record data sheet by the field crew. The back of the form can be used if additional space is needed.

The Surface Water Chemistry Long-Term Monitoring Record data sheet will indicate the tag number for any tag previously placed on a tree adjacent to the collection site. For sites with tags, the access notes will indicate the location and provide a description of the tag tree. In some cases, previously placed tags may have disappeared. If the tag is missing, the field crew should replace the missing tag before leaving the site or make a note for future tag replacement.

Ideally, site photos will provide upstream and downstream views of the sampling site, as well as views of the tag tree. If site photos are not available, photos should be obtained by the field crew as described in section 3.3.2.

3.3.2 Establishing New Sampling Sites

Note: avoid disturbance of water upstream of the sampling point before sample collection by performing site documentation steps (placement of site tags and site photography) after sample collection.

Site maps and access notes should indicate general or preliminary sampling site locations for new sites. The 6th level HUC folders for the sample sites will include USGS 1:24,000 quadrangle maps, as described above (section 3.3.1) for location of previously established sites and a GIS maps will be provided (see Figure 1) that indicates approximate sampling site locations. In either case, it will be the responsibility of the field crew to select and document the specific sampling site locations based on conditions observed in the field. The field crew should consider the following guidelines:

- Sample sites should be readily identifiable by reference to permanent-type landmarks such as confluence points of major tributaries, well-marked boundary lines, and stream crossings by permanent roads or well-marked trails.
- Sample sites should be selected to avoid direct runoff from roads and trails, as well as unmixed flow from tributaries. This will be achieved for most sites by sampling sites 25 yards above road or trail crossings, or 25 yards above or below inflowing tributaries.
- The best point to sample will be where the water is flowing fast or falling, where there are no eddies, and where the depth is at least six inches. Ideally the sampling

point is one that can be reached during most flow conditions while kneeling on the stream bank or on stable rocks downstream from the sampling point. It should not be necessary to stand in the water to reach the sampling point.

The field crew will need to provide detailed site documentation for new sites. Site documentation consists of maps, access notes, site tags (for permanent plots), site photos, site elevation, and other items described in section 3.3.3 below. Preparation of site documentation for new sites should include the following steps:

1. Record additional information to clarify preliminary site and access descriptions in the space provided on the Surface Water Chemistry Long-Term Monitoring Record data sheet. Use the back of the form if additional space is needed for access description. Use the back of the form to draw a site-sketch map.
2. At monitoring sites, place site tags on a vigorous streamside tree of at least 6 inches diameter. The tag should be nailed with a small hammer on the downstream side of the tree a few inches above ground level. The nail should not be driven all the way in; leave about ¼ inch to allow for tree growth. Record the tag number, the tag location, the tag tree species, and the tag tree diameter at breast height in the **Field Notes and Observations** portion of the Sample Information section provided on the Surface Water Chemistry Long-Term Monitoring Record data sheet. It will be helpful to draw a map (including bearing and distances) detailing the relationship between the tag tree and the stream sampling site. *Do not place tags on trees in National Forest Wilderness Areas and do not place tags on trees on private land without permission.*
3. Record additional information to clarify preliminary site and access descriptions in the space provided on the Surface Water Chemistry Long-Term Monitoring Record data sheet.
4. Obtain sampling site photos showing the upstream and downstream views from each site. At the sites selected for monitoring the photos should include, in one lower corner of each photo, a large-print card on which is indicated the site ID code for that site. Photos should also be taken to include distinctive streamside features such as particular rocks and trees. Orange flagging should be placed (temporarily) on the tag tree to allow its identification in the photos. More distant views can be taken to provide perspective. Provide picture numbers in the **Field Notes and Observations** portion in the Sample Information section on the Surface Water Chemistry Long-Term Monitoring Record data sheet.
5. Determine site geographic coordinates if a survey grade GPS unit is available. Follow the GPS instructions to obtain the most precise readings that can be obtained with the unit. The units for projection will be a geographic projection (NAD27) recording the outputs in decimal degrees. Record the site coordinates in the **GPS Latitude** and **GPS Longitude** spaces in the Sample Information section provided on the data sheet.

3.3.3 Completing the Site Information Section of the Data Sheet

The only item needing to be completed before leaving the stream sample site is the **Stream Name** (taken from the 1:24,000 quadrangle map) and **Location Description**, but the field crews can also fill in the **National Forest**, **Ranger District**, **Wilderness**, and **Other Administrative Name** (such as if the sample was taken in a Research Natural Area, Experimental Forest, or campground).

Site Information

Stream ID		Stream Name	
Latitude	Longitude	Location Description (e.g., west side of lake near weir)	
Hydrologic Unit Code		National Hydrography Data (NHD) Reach Code	
National Forest		Wilderness	
Ranger District		Other Administrative Name (e.g. Research Natural Area, Experimental Forest)	
Elevation (m)		Stream Order (N/A for lakes)	Lithology
Catchment Slope (%)	Catchment Aspect (e.g., N, SW, NE)		Catchment Size (ha)
% of Catchment above the Sample Site:	Hardwoods__	Conifer ____	Exposed Bedrock Or soil ____
		Meadows/ Shrubs ____	Other ____

The remaining site information will be completed after conducting the fieldwork with the aid of the ArcMap and Spatial Analyst® software. First, the project manager will compare where the sample sites were planned to be established (using ArcView® or ArcMap®) with the location plotted by the field crews on 1:24,000 quadrangle maps (see **Establishing New Sampling Sites** above). Examining the 1:24,000 quadrangle maps will also provide the information needed to complete the **Stream Name** and **Stream Order**. Some proposed sites may have not been sampled and need to be deleted from the spatial coverage; while others sites will need to be moved to where the actual sampling occurred. Once the sample site point coverage has been edited then the XTools utility will be used to calculate the latitude and longitude values. These two numbers will then be carefully recorded on the **Latitude** and **Longitude** portion of the datasheet. The **Stream ID** is a 13 character code combining the first seven numbers of the longitude and the first six numbers of the latitude. Sites located less than 100 degrees longitude will have a “0” used in the first character place and there will be no minus character in the Stream ID name.

The Select Feature tool in ArcMap can be used to select the HUC containing the sample points. The HUC value (character) can then be copied and pasted into a column (within the site point shape file that has been labeled HUC) using the Calculation Option which appears by selecting the HUC column with a right click of the mouse button. Of course it may be necessary to create the HUC column first in ArcCatalogue® before the editing can be completed.

The National Hydrography Data (NHD) Reach Code should be entered on the datasheet if the streams have been routed to use in the Natural Resource Information System (NRIS)

Aquatics database for the 1:24,000 scale hydrology layer. This will require using the GIS tool within the NRIS Aquatic database and adding the stream chemistry site point shape file to the ArcView project. Determine the NHD Reach Code by highlighting the stream coverage name in the legend. The identify tool in ArcView can then be used to determine the NHD Reach Code by using the identify tool on each of the points representing a sample site where a stream sample has been collected.

The value for the **Lithology** is determined by using the identify tool to determine what lithology type is present at each of the sample points. Using the Zonal Statistic option in Spatial Analyst along with a 10 or 30 meter digital elevation model (DEM) will provide an estimate of the **Elevation** for each sampling location.

Next, it will be necessary to digitize within ArcMap the topographically-defined contributing or source area for that point in the stream (see Figure 2). This will be referred to as the catchment or watershed. Be sure to also include the appropriate HUC number and Stream ID in the catchment shape file database. The catchments are drawn with the aid of a 10 or 30 meter DEM overlaid on a hillshade map, tin coverage, and/or contour interval map developed with Spatial Analyst (see example below).

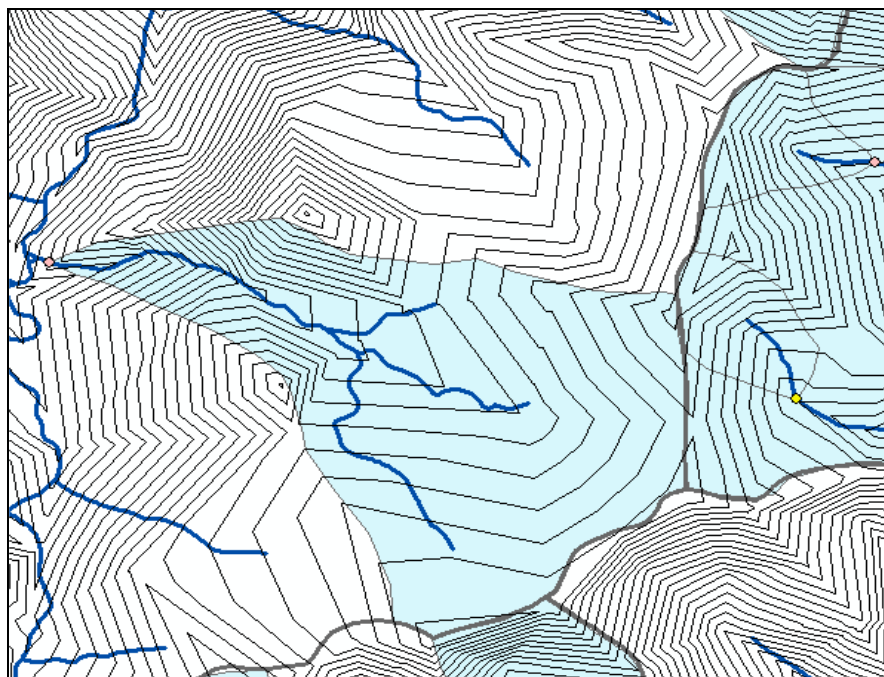


Figure 2. Catchments (light blue polygons) drawn in ArcMap for each sample point with the streams (blue lines), HUC boundary (gray lines), and contours (black lines) derived from a 30 meter DEM.

The remaining values are estimated using the catchment boundaries. The XTool utility is used to estimate the **Catchment Size** in hectares. The **Catchment Slope** is the average (mean) percent slope in the catchment, but first it will be necessary to use Spatial Analyst to derive the percent slope for the area of interest using the 10 or 30 meter DEM. Similarly, the **Catchment Aspect** is also derived using the 10 or 30 meter DEM and the average (mean) aspect is calculated

using the Zonal Statistic option in Spatial Analyst. The average **Catchment Aspect** is then placed into one of the following categories:

337.5 – 22.5 = N	22.5 – 67.6 = NE
67.5 – 112.5 = E	112.5 – 157.5 = SE
157.5 – 202.5 = S	202.5 – 247.5 = SW
247.5 – 292.5 = W	292.5 – 337.5 = NW

The catchments can be examined with digital aerial photographs to estimate the percentage of the area above the sample site that is occupied by trees, exposed bedrock, meadow/shrubs, open areas, or other categories.

3.4 Sample Collection, Handling, and Documentation

3.4.1 Preparing for the Stream Sampling Trip

Obtain HUC folders for the sites to be sampled. The Surface Water Chemistry Long-Term Monitoring Record data sheet should be completed to the extent possible prior to the sampling trip. For previously established sites, the Site Information, tag number, and description of the tag tree should be filled out on each form. The following are the additional steps that need to be completed before going to the field:

- Obtain one sample bottle for each site to be sampled. Preprocessed bottles filled with deionized water should be provided by the analytical lab as indicated in Section 3.2.3. Ideally the bottles will have a blank label tape affixed to the bottles.
- At least three additional preprocessed sample bottles will be required for each sampling trip, one for use as a duplicate sample and two for obtaining a process blank. One in about every 10 sites sampled should be selected for duplicate sampling and a blank sample. This sampling will generally occur at the first site after the noon time meal.
- Obtain frozen refrigerant. Be sure the refrigerant has been in the freezer at least two days prior to the day of sampling. Place the refrigerant in a securely sealed plastic bag in the insulated container(s) that will be used for sample holding and transport. Provide enough refrigerant to keep the samples cold until delivery to the lab or until placement in a refrigerator if samples are to be stored before shipping.
- Transport the water sample bottles, including the duplicate bottle and the process blank bottle, in the cooler that will be used to store the samples.

3.4.2 Stream Sample Collection Procedure

Sampling should be avoided during abnormally low or high runoff conditions in order to obtain samples representative of common watershed conditions. USGS data (for example, North Carolina data are found at: <http://nc.water.usgs.gov/info/h2o.html>) can be examined prior to

going to the field to estimate current stream flow from stream gauges in the area of the sample site. This precaution is more important when watershed characterization will be based on single samples rather than multiple samples collected at different times. MAGIC modeling is generally based either on annual average or spring baseflow water chemistry. The former requires intensive monitoring data collected throughout multiple years. The latter requires only one or a few samples collected during spring. In general, it is preferable, but not necessary, to base the modeling on multiple samples (either collected throughout the annual cycle or just during the spring season) collected over several years. MAGIC can be calibrated to monthly values, but is not an appropriate tool with which to examine episodic (storm-driven) processes. Often, the magnitude and frequency of episodic acidification is considered as an item separate from the modeling. In other words, MAGIC is used to project annual average or spring baseflow chemistry, and the probable extent of episodic acidification is assessed independently for both current and future conditions.

As described above (Sections 3.3.1 and 3.3.2), locate the sampling site and determine the exact sampling point in the stream. Carefully avoid disturbance upstream of the sampling point prior to sample collection. This means not walking in the upstream water or on upstream rocks.

Collect the sample on a step-by-step basis, as follows:

1. Open the cooler containing the sample bottles.
2. Remove the gloves from the plastic bag and put them on.
3. Remove the sample bottle from the cooler. Do not put the sample bottle on the ground.
4. The sample bottle will be filled with deionized water. Pour this out at a location below the site selected for sampling and bottle rinsing.
5. If the sample bottle has not been prelabeled, use a permanent ink felt marker to add the site identification code and date to the affixed label tape. Label sample bottles prior to actual sampling, as wet bottles are difficult to label.
6. Walk carefully to a place 2 to 3 feet below the sample site. Rinse the sample bottle in the stream at a location 2-3 feet below the sample collection point. The bottle and cap should be rinsed 3 times. For each rinse, fill up the bottle and then pour the rinse water over the inside of the cap, held bottom-side up in the other hand. Pour the rinse water downstream of the rinsing and sampling points and avoid stirring-up streambed debris during the process.
7. After the rinsing is completed, move to the sampling point and collect the sample. Fill up the bottle as completely as possible, but note that it may be impossible to avoid a small air space in the bottle. While collecting the sample, avoid stirring-up streambed debris that might be collected with the sample. Also avoid collecting water that has come in contact with the gloves or the outside of the bottle. This can be best achieved by sampling rapidly flowing or falling water.
8. Immediately after collecting the sample, place the lid on the bottle (tightly) and return the bottle to the cooler. We recommend placement of the sample bottle back

into a zipper-lock bag prior to putting the bottle in the cooler. Do not place the sample bottle on the ground.

9. Immediately repeat the above steps for any duplicate samples. When duplicate samples are collected, the bottles should be labeled with the **Sample ID** and Duplicate 1. About one site in 10 will be selected for a duplicate sample, which can be the first site sampled after the noon time meal.
10. Select about one site in 10 for preparation of the process blank sample, immediately subsequent to collection of the duplicate sample. Pour a bottle containing deionized water into a second bottle that is emptied of its deionized water in the field. This second bottle should be considered and analyzed as a process blank.
11. Obtain the temperature of the stream water by submersing the thermometer (or pH probe) in the stream water until the reading is stable. Take the reading while the bulb of the thermometer (or pH probe) is in the water. Record the temperature to the nearest 0.5 degree C.
12. If pH and conductivity readings are to be obtained in the field, follow the procedures cited in section 3.5. The pH meter should be calibrated at each sample site with pH 4.0 and 7.0 buffer solutions. Because calibration of the pH meter is time consuming and because pH measurement can be difficult in the field, some investigators choose to not measure pH in the field, but rather to rely on subsequent laboratory analyses. It should be noted, however, that stream impairment listings might require field measurements.
13. Complete the Sample Information and Field Measurement sections on the data sheet while at the sample site (see Appendix B for further instructions).

Note: at some point during the sampling trip when the field team is at a sampling site, the bottle designated to be a process blank should be removed from the cooler, emptied of its deionized water, and refilled with deionized water from another bottle. This refilled bottle should be labeled "Process Blank." This bottle should then be placed back into a plastic bag, or otherwise treated as the actual samples, and returned to the cooler. A good time to prepare the process blank would be when the duplicate samples are collected.

3.4.3 Sample Handling

- Place collected samples in an insulated container with refrigerant within 15 minutes of collection.
- For sites that are close to road access, the insulated container for samples can be left in the field team's vehicle. The sample should be placed in the container upon return to the vehicle.
- For sites that require longer hikes (greater than 15 minutes), the collection team should make arrangements to keep the sample cold during the return hike. The recommended approach is to use an insulated container that will fit in a backpack.

- The samples will be stable for most analyses as long as they are kept on refrigerant or in a refrigerator until delivery to the lab. The refrigerant may need to be replenished during sample transit. Do not place the sample bottle in a refrigerator or container with food or in any container that is not clean.
- Samples that are to be shipped to the analytical laboratory will be packed in insulated shipping containers with frozen chemical refrigerant. The refrigerant should be packed in double zipper-lock bags.
- Overnight delivery will be used to ship the samples to the lab as soon as practical after sample collection. Ideally, a cooler full of samples is prepared for shipment each morning before going to the field to collect more samples. Ideally, samples should not be collected on Fridays or on days preceding a holiday when the laboratory will be closed. Samples collected on Friday must be held until Monday before they can be shipped. Check with the laboratory regarding recommended sample holding times.
- The Chain of Custody Form (used to maintain a record of sample custody until receipt at the analytical lab) must be completed for the samples in each shipment and a photocopy of the completed form will accompany the sample. The original will be stored in the HUC folder. An example of the Chain of Custody Form is provided in Appendix B.

3.5 Stream Water Laboratory Analysis

Application of the MAGIC model requires analyses of 10 stream water constituents:

- acid-neutralizing capacity (ANC)
- pH (lab, and if desired, also field measurement)
- 3 acid anions: sulfate, nitrate, and chloride
- 4 base cations: calcium, magnesium, potassium, and sodium
- ammonium

Conductivity should also be measured for purposes of quality assurance. If MAGIC is to be used to estimate future pH, then it will also be necessary to measure dissolved organic carbon, and if pH is below 5.5 to determine total monomeric aluminum and organic monomeric aluminum. If pH is below 5, it is also recommended to measure total fluoride, which will be needed to calculate aluminum speciation.

The following sections describe methods for sample bottle preparation, sample filtration, sample analysis, and quality assurance. These methods are appropriate for analysis of low ionic-strength stream waters associated with forested mountain watersheds in the southern Appalachian Mountain region. Although data obtained by the described methods have been successfully used for other acidification effects assessments and trend monitoring programs conducted in the region, the described methods are specifically proposed here for purposes of supporting an assessment of watershed health on FS lands in the upstate of South Carolina, eastern Tennessee, and western North Carolina. Other methods, as described by other protocols listed in Appendix A, may also be appropriate for this and other purposes.

The critical factors for use of this or other protocols for water quality analysis include documentation of collection and analytical methodology and quantitative determination of accuracy and precision.

3.5.1 Sample Bottle Preparation

Sample bottle preparation will involve a triple rinsing of each 250 ml bottle with deionized water. The bottles will then be stored overnight, or longer, filled with distilled water, followed by a final rinse with deionized water. Finally, each bottle will be filled with deionized water before shipping to the project location. Treating the sample bottles in this manner maximizes the likelihood of achieving a conductivity for a blank sample that is less than the acceptance criterion of <1.2 uS/cm.

3.5.2 Sample Filtration

All samples are normally filtered using a 0.45 micrometer polyvinylidene fluoride filter as soon as possible after arrival at the laboratory, to remove particulate matter. The ion chromatographs have microbore tubing which can clog easily if even a small particle makes it's way into the tubing. Therefore, samples are kept cold and analyzed as soon as possible after arrival. The samples continue to be kept refrigerated for possible further analysis even after the initial analysis and QA process.

3.5.3 Sample Analysis

Currently, the USFS/USGS Water & Soils Lab in Fort Collins Colorado performs the chemical analysis for the stream water samples (<http://www.fs.fed.us/rm/waterlab/Labprotocols.htm>). The following is a summary listing of instrumentation and techniques employed for sample analysis. Equivalent instrumentation and techniques can be substituted, such as those employed by the University of Virginia (see Appendix C). A listing of other protocols and methods can be found in Appendix A.

pH (hydrogen ion)

Instrumentation: PC-Titrate (Man-Tech Corp.) Autotitration system for pH and alkalinity
Technique Summary: Gran analysis technique (Gran 1952)

Reporting units: standard pH units

Acid-Neutralizing Capacity

Instrumentation: PC-Titrate (Man-Tech Corp.) Autotitration system for pH and alkalinity (acid-neutralizing capacity)

Technique Summary: Gran analysis technique (Gran 1952)

Reporting units: $\mu\text{eq/L}$

Conductivity

Instrumentation: PC-Titrate Conductivity Meter Model 4310 for conductivity

Technique Summary: Electrometric (Standard Methods for the Examination of Water and Wastewater, APHA, 20th Edition, 1998)

Reporting units: $\mu\text{S}/\text{cm}$

Sulfate, Chloride, Nitrate

Instrumentation: Waters IC with Dionex AS12 A Separator Column, Model 431 conductivity detector, Model 717 plus autosampler, Model 510 pump

Technique Summary: Ion Chromatograph (IC) with separator column for anions (APHA 1998a)

Reporting units: $\mu\text{eq}/\text{L}$

Calcium, Magnesium, Potassium, Sodium

Instrumentation: Waters IC with Water IC PAK Cation M/D Column, Model 431 conductivity detector, Model 717 plus autosampler, Model 501 pump

Technique Summary: Ion Chromatograph (IC) with separator column for monovalent/divalent cations

Reporting units: $\mu\text{eq}/\text{L}$

Fluoride

Instrumentation: Waters IC with Dionex AS12A Separator Column, Model 431 conductivity detector, Model 717 plus autosampler, Model 510 pump

Technique Summary: Ion Chromatograph (IC) with separator column for anions (APHA 1998a)

Reporting units: $\mu\text{M}/\text{L}$

Aluminum, total monomeric and organic monomeric

Instrumentation: Not analyzed at the Fort Collins lab (see Appendix C)

Dissolved organic carbon

Instrumentation: Not analyzed at the Fort Collins lab (see Appendix C)

3.5.4 Data Quality

The quality control and assurance component of stream water sample collection and analysis should include analysis of reference standards, field duplicates, and process blanks, as well as examination of charge balance and measured versus calculated conductance differences.

Quality control in the field can be achieved by careful site location and close adherence to sample collection and sample handling procedures.

Quality control in the lab can be achieved by close adherence to sample bottle preparation procedures and instrument operation and calibration procedures. In addition, reference standards of known concentration should be distributed among the samples to be analyzed. These should include synthetic mid-range standards and natural-matrix reference standards. When values obtained for the standards deviate from established mean values by unacceptable amounts (typically 5% or 2 standard deviations), analysis results for the associated samples should be disqualified. Additional aliquots should be prepared for reanalysis if necessary. In the event that acceptable reference sample values cannot be obtained, the data records for associated samples should be flagged in the database.

Quality assurance should be provided by analysis of results for standards and duplicates.

Analytical accuracy should be determined by analysis of both synthetic and natural-matrix reference samples with analyte concentrations in the range of the sample concentrations. During the analysis process the reference samples should be distributed among the survey samples. Reference samples should represent about 5 to 10 percent of the total number of samples analyzed, with at least one reference sample included in each analysis session. Results of reference sample analysis should be reported for each analyte as the mean and standard deviation of the difference from the nominal concentration values.

Data precision should be determined as combined sampling and analytical precision. Approximately 10% of all samples should be collected in duplicate, with at least one duplicate set included in every sampling trip. The duplicates should be distributed randomly among the samples for analysis. Results should be reported for each analyte as the mean and standard deviation of the absolute difference between duplicate sample pairs.

Quality assurance should also involve analysis of process blanks. These should be sample bottles that have been prepared and filled with deionized water in the same manner as bottles used for sample collection. As indicated in section 3.4.1, two extra bottles should accompany each sample team on each sampling trip. In the field, the deionized water in one will be discarded and replaced with the deionized water in the other. The deionized water sample becomes the process blank. The process blank bottle should be included with the actual sample bottles that are delivered to the lab. Analysis of the deionized water in this bottle will provide a measure of error associated with the complete bottle preparation, sample handling, and analysis process. Results of process blank analysis should be reported for each analyte as the mean and standard deviation of the process blank analyses.

Charge-balance and conductance differences should also be determined for the analysis of all samples. These checks, which provide information about complete sample analysis, are commonly used to indicate analytical error or the presence of unmeasured ions.

Charge balance error is a measure of deviation from charge equivalence for anions and cations. Percent charge balance error for samples is defined as $100 \times (\text{sum cations} - \text{sum anions}) / (\text{sum cations} + \text{sum anions})$. Charge balance error should not exceed 15%, except where dissolved organic carbon concentration is high ($> 5 \text{ mg/L}$).

Determination of conductance difference involves comparison of measured conductance (corrected to 25 degrees C) with the sum of the specific conductances of the measured ions. Percent conductance difference is calculated as the $100 \times (\text{calculated conductance} - \text{measured conductance}) / \text{measured conductance}$. Conductance difference should not exceed 30%.

Analytical records for samples that exceed the criteria for charge balance error or conductance difference should be carefully examined for possible causes. Any analyte that is identified as suspect should be reanalyzed. If the problem cannot be identified or corrected, the sample analysis record should be flagged.

3.6 Stream Water Data Management

The completed datasheet will be entered into the Forest Service corporate database called the Natural Resource Information System (NRIS). A photocopy (make sure all of the entries are clearly legible) of the data sheet is sent (along with any helpful electronic files) to the Air Resource Management water chemistry data manager. Currently, that person – MS. Barb Gauthier – resides in Fort Collins, CO. The water chemistry data manager will enter the field data into NRIS, make sure the lab analysis results are correctly merged with the field data, and perform quality assurance on the data to make sure the chemical results are reasonable.

Appendix B provides the FS water chemistry data sheet entitled “Surface Water Chemistry Long-Term Monitoring Record” and instructions for completing the datasheet. Also, included are the “Chain of Custody” forms to be completed and sent with the water samples to the laboratory.

4.0 SOIL DATA COLLECTION

4.1 Arrangements with the Soil Chemistry Laboratory

Appropriate agreements or contracts will need to be made with a qualified soil chemistry laboratory well in advance of field sampling. Currently, the USFS Soils Lab in Grand Rapids, Minnesota has been chosen to perform the analyses on soil chemistry samples collected in the National Forests of western North Carolina, eastern Tennessee and the upstate of South Carolina.

4.2 Sampling Materials

Each field crew should be provided the following equipment and materials, except as noted:

- Site information folders (including maps and Soils Field Data Forms)
- Site documentation materials
- Sampling protocol (this document)
- Sampling equipment (shovel, spade, folding saw, trowel, and/or pruning shears)

- Half-gallon plastic ziplock-type plastic bags
- Backpacks
- Digital camera with extra memory card and battery
- Survey grade global positioning system and compass
- Small tape measure and 50 or 100 meter tape and/or small laser range finder
- Small water bottle
- Hydrogen peroxide to check for the presence of Mn concretions (optional)
- Clinometer
- Golf tees painted bright orange for photographing horizon designation breaks
- Munsell color book
- NSSC Field guide for describing soils (optional)
- Picking knife for cleaning the profile and digging out samples in thin horizons
- Large-print cards with site identification code for photographs

More details on equipment and materials follow in sections 4.2.1–4.2.4. Instructions for use are in sections 4.3 and 4.5.

4.2.1 Site Information Folders

The soil samples taken for acid-base chemistry on National Forest lands in North Carolina, South Carolina and Tennessee will be collected within stream catchments where one or more water chemistry samples have been taken. The catchments will likely be selected for study within a designated Wilderness, or 6th level HUC. The 6th level HUC was chosen as a unit of analysis because the Forest Service may own an appreciable percentage (20 percent or more) of some of these watersheds. Each sampling site's information will be placed in the appropriate HUC folder and will include the Soils Field Data Forms (see Appendix D), site maps, and other site documentation.

Maps will include 1:24,000 USGS quadrangle maps with sampling sites identified and Forest recreation maps to help navigate to the area. Maps generated using GIS will also be included to show where the project manager has selected potential sites to sample. Typically, at least one plot will be planned in each vegetation cover, and soil map unit and/or lithology; and is within 200 meters of the stream and positioned at a mid-elevation in the catchment.

Site documentation may be incomplete at the time of sampling for sites that have not been previously established or for sites that were established following different protocols. Site documentation information will be maintained in the NRIS database for purposes of record keeping, as described in section 4.6.

Site documentation information in the HUC folders should include site maps, narrative access descriptions, site coordinates and elevation, site-tag numbers and locations, site photographs, and sheets or index cards with site identification codes (2 for each site) in large print for use in site photographs.

Soils Field Data Forms serve for documenting sample locations and sample collection. These forms should be printed on waterproof paper. A copy of the Soils Field Data Form is provided in Appendix D.

4.2.1 Site Documentation Materials

Site documentation materials include uniquely numbered aluminum tags, nails and a small hammer for tag placement, flagging tape, a camera for site photographs, a survey grade GPS unit for determination of geographic coordinates and a large-print site identification label or card for placement in the soil pit when taking the photograph of the soil profile. Pencils and waterproof pens are also required.

4.2.2 Soil Sampling Equipment

Sampling material includes digging, measuring, and soil handling equipment. Digging equipment should include a heavy-duty hand trowel and a “sharpshooter” shovel with a 30-inch steel or fiberglass handle and an approximately 5.5-inch wide, 18-inch long blade. A small folding saw should be included to cut around the perimeter of forest floor samples and/or a pruner to cut large roots.

Measuring equipment should include a tape measure with metric units (and perhaps English units also) and a length of at least five meters.

Soil handling equipment should include a small plastic tarpaulin (about 4' x 6'), and sample bags. The sample bags should be heavy-duty half gallon sized zipper locked type plastic bags. In addition, dry paper towels should be available for cleaning soil from the tarpaulin and digging equipment between samples.

4.3 Establishing Sampling Sites

All soil sampling sites will be newly established for purposes of the current program. Site maps and access notes should indicate general or preliminary sampling site locations. The site maps may include Forest Recreation maps and USGS 1:24,000 quadrangle maps. GIS maps will be provided that indicate approximate sampling sites locations. In either case it will be the responsibility of the field crew to select and document the specific sampling site locations based on conditions observed in the field. The field crew should consider the following guidelines.

Sample sites should be selected to represent the typical landscape (aspect, slope, and vegetation type). Avoid selecting sites that are:

- Near abrupt changes in landscape condition (aspect, slope, and vegetation type).
- Located where it is apparent that soil has been removed or deposited by erosion or downslope movement.
- Characterized by substantial soil disturbance due to tree-throw or other major disturbances.

- Located in seepage areas, runoff concentration areas, or locations that are otherwise wetter than the surrounding landscape.
- Areas that do not represent the soil type mapped by a recent USDS-NRCS Soil Survey if available (because this may be an inclusion that is not typical for the map unit).

The sample-collection team will need to provide detailed site documentation. Site documentation consists of maps, access notes, site tags, site photos, site elevation, and geographic coordinates. Preparation of site documentation for new sites should include the following steps:

1. Record additional information to clarify preliminary site and access descriptions provided on the Soils Field Data Form. This can include drawing a site-sketch map. Use the back of the form when needed.
2. Access notes should describe the route to the site and the location of the site. In most cases, the access notes should describe a point of departure from an identifiable location on a road, trail, or stream course. The access notes should indicate the compass bearing and approximate distance from the point of departure from an identifiable location to the site location.

Determine the geographic coordinates of the sampling site. Follow instructions to obtain the most-precise readings that can be obtained with the GPS unit. The units for geographic coordinates (NAD27) will be decimal degrees. The elevation (taken from a 1:24,000 quadrangle map) and geographic coordinates of the sampling site should be recorded on the Soils Field Data Form.

3. Place a site tag a few inches above ground level on a vigorous nearby tree of at least 6-inches diameter. This tag should be affixed to be visible upon approach from the nearest trail or road. The nail should not be driven all the way in; leave about $\frac{1}{4}$ inch to allow for tree growth. The tag number, the tag tree species, the diameter at breast height of the tag tree, and the distance and compass bearing from the specific sampling site should be recorded on the Soils Field Data Form.
4. Obtain sampling site photos of the site surroundings. One member of the collection team should stand at the sampling site and hold up a large-print site identification label (provided in the site folders) for the photos. Orange flagging should be placed (temporarily) on the tag tree to allow its identification in the photos. Photos should be taken to include distinctive features of the sampling site such as particular rocks and trees. Indicate the number of pictures taken in the space provided on the Soils Field Data Form.
5. Obtain sampling site photos of one face of the soil pit. After the soil pit has been excavated to its maximum depth, square off one representative face using the shovel, and photograph (using the flash unit) the face of the pit to show horizon development. Within the field of view, place an identification label and a tape measure to indicate depth measurements.

The site documentation described above will facilitate return visits to the sampling sites if repeated sampling is contemplated or if decisions are made later to conduct repeated sampling. Given that soil sampling is “destructive,” a sample should not be collected at the same specific location as a previous sample. A simple solution to this problem would involve treating the initial sampling site as the center of a sampling plot. Any repeat sampling can be conducted at fixed distances in an array around the central site.

4.4 Sample Collection, Handling, and Documentation

MAGIC is calibrated using data for mineral soils, generally by designating either one or two soil layers. These do not necessarily correspond with horizon development. The top 10 or 20 cm of mineral soil is commonly collected, and is thought to represent the source areas for relatively quick flow. Deeper mineral soil samples (for example 10 to 50 cm mineral soil depth) are often also used, and are thought to represent the source areas more typical of base flow water chemistry. Soil sample depth is kept constant from site to site and is generally not adjusted for differences in horizon thickness. Soils acid-base chemistry conditions are used to constrain the model behavior, but the principal constraint on model output is the drainage water chemistry to which the model is calibrated.

Data for organic soil horizons are generally not used as part of the modeling effort, but can provide valuable information regarding nutrient dynamics and nitrogen cycling. In addition, the nitrogen components of the model are in flux and may be expected to change in the near future. Thus, collection of O-horizon data is recommended. This material can be archived and analyzed at a later date, if desired.

4.4.1 Sample Collection Procedure

- Avoid sampling during precipitation or when the soil is wet from recent precipitation. (This does not include soils that are naturally wet and have high seasonal water tables.)
- Avoid contact between skin and the soil being collected by being careful in sample collection and/or wearing plastic gloves while conducting the sampling.

Collect samples on a step-by-step basis, as follows:

1. Use the shovel to remove and discard all of the loose forest-floor material (litter) from an area 70 cm in diameter at the sampling site. Do not remove any organic matter that is adhered to the underlying material.
2. Use the shovel and saw or pruners to collect the O-horizon (organic soil horizon) from the 70 cm-diameter sampling circle. Place the organic soil matter on the plastic tarpaulin and thoroughly homogenize manually using the trowel. Place this material in a soil sample bag and seal the bag. Use a permanent-ink marking pen to label this bag, indicating the site identification code, the date, and “O-horizon Sample.” If the O-horizon material is too thick to allow collection of all material in one bag, select a sampling circle smaller than 70 cm in diameter, and record this deviation in the sample log.

3. After removal of the forest floor and O-horizon material, wipe off the plastic tarpaulin with a piece of paper towel to remove excess O-horizon material, and use the shovel to dig a 70-cm diameter sampling pit to approximately 10 cm from the top of the mineral soil (interface between the O-horizon and the mineral soil). The material removed from the pit should be placed on the plastic tarpaulin and thoroughly homogenized manually using the trowel. Add homogenized soil, excluding rock fragments, to a sampling bag (approximately 500 grams of soil is needed) until the bag is about three-quarters full. Seal the zip-lock type bag and then place the sample bag inside of another zipper-lock type plastic bag.
4. Label the bag, indicating the site identification code, the date, and “Shallow Sample.”
5. Set the remaining soil and rock material on the tarpaulin aside.
6. Dig the soil pit deeper (if possible to 50 cm or deeper from the top of the mineral soil; 40 cm below the bottom edge of the Shallow Sample that you just collected). The material (10 to 50 cm depth mineral soil) removed from the pit should be placed on the plastic tarpaulin and thoroughly homogenized manually using the trowel. Add soil, excluding rock fragments, to a sampling bag until the bag is about three-quarters full. Seal the bag with a twist tie. Label the sample bag, indicating the site identification code, the date, and “Deep Sample.”
7. Measure the depth and diameter of the mineral soil sampling pit and record on the Soils Field Data Form.
8. Estimate the percent rock fragments by volume for both the shallow and deep sample depths and record on the Soils Field Data Form.
9. Return all remaining soil and rock fragments to the sample pit and cover with debris. If desired, it might be useful to collect and retain a small sample of the characteristic rock materials (fresh piece(s) a few inches in diameter, or large enough to handle easily).
10. Place each soil sample bag inside a second, outer plastic bag containing the site identification label used in the photographs or other piece of paper on which is written the site identification code.
11. Complete the Soils Field Data Form while at the sample site.
12. Determine if a duplicate soil sample is needed at this site. If so, dig a second pit in close proximity to the first, and repeat all sampling steps.

4.4.2 Sample Processing

Sample processing involves drying the samples and removing material greater than 2 mm in size. Sample drying and sieving of the soil samples can be done by the field crew at a staging area or at the laboratory. In general, we recommend transporting the samples as quickly as possible to the laboratory for processing. Process the samples following these steps:

1. Soil samples in clean plastic bags should be shipped with ice packs to the lab for analysis, via one-day or two-day delivery service. Shipments should not be sent to arrive at the end of the week or on a weekend when laboratory personnel will not be available to begin processing. The lab should be consulted to determine necessary sample amounts. The bags for sample shipment to the lab should be labeled indicating the site identification code, the sample collection date, and either “O-horizon (#299,xxx)”, “Shallow Sample (#300,xxx)”, or “Deep Sample (#305,xxx),” as appropriate. If the samples will not be shipped to the laboratory within two days of collection, they should be placed on a bench top in a cool room, out of the sunlight, and stored with the bags open at the top to allow for air movement. Reseal the bags and place them in a cooler with ice packs immediately prior to shipping. Some samples might be from states that have restrictions on soil movement because of potential infestation by golden and corn cyst nematodes, imported fire ants, and witchweed. This restriction is under the jurisdiction of the USDA Animal and Plant Health Inspection Service (APHIS) Plant Protection and Quarantine Program. A map of regulated states can be found at the APHIS website (<http://www.aphis.usda.gov/ppq/maps/soil2002.pdf>). Field crews sending regulated samples must label the containers “Contents Soil Samples,” include a copy of the soil permit, and display a PPQ Form 550 on each sample (the form can be found at: <http://www.aphis.usda.gov/ppq/permits/soil/index.html#process>).
2. Ten percent of the samples should be selected for duplicate analysis. For these samples, two bags for each of the three soil layers collected should be prepared for shipment to the analytical lab. The duplicates should be collected from separate pits located in close proximity, designated “1” and “2,” and labeled accordingly.
3. The receiving lab is required to hold an APHIS permit to receive and handle regulated materials. The preparation crew should check the front entry each day for new samples. Any new samples should be opened and preparation begun on the day of receipt, or placed in the walk-in cooler for preparation on the following work day. Make a photocopy of the shipping form for use in the headhouse and store it in the notebook labeled “Atmospheric Deposition Effects (ADE) Shipping Forms.” Give the original to the soils supervisor. *ADE field crews should alert the lab to incoming samples by mailing or emailing a copy of the shipping form prior to shipping samples. The preparation crew should place this form in a “pending” file, then attach it to its mate that should arrive with the samples.* In the headhouse, open boxes and sort new samples by site identification and horizon (O, Shallow, or Deep). Print sample labels using software on the headhouse PC. The sample number scheme is ADE-number (e.g. ADE-300001). Affix labels to each new sample and record the bag label and shipping form information in the hard-copy notebook labeled “ADE Incoming Soils.” **Fill all columns to create a complete paper trail.** Make a note if data is missing and, **at least daily**, copy all information from the hard copy into the MS Excel workbook found on Server1 in folder ADE2004. Do not add, delete, or modify spreadsheet columns without approval from the soils supervisor. Select a plastic drying container and label it with sample ID, date, and type of soil (mineral or organic). Zero the balance, then weigh the container and record the weight in “Tare (g)” column. Zero the balance again with the container in place. Empty the sample into the container, weigh, and

record the weight in the “Field Moist – Tare (g)” column. Cut bag labels from the sample bags each day and put them in numerical order and store. These are kept permanently.

4. Place sample in soil drying room and, if possible, keep all samples from each state together to facilitate removal. Run the dehumidifier and keep the door closed. Samples are considered air-dry with no more than 5% weight loss overnight. Sweep drying room weekly.
5. Remove from drying room if weight loss is less than 5% overnight. Zero the balance, weigh the container and sample, and record the weight in the “AD + Tare (g)” column.
6. Dry mineral soil should be passed through a 2-mm sieve without forcing material through the sieve. Using a mortar and pestle, break clods (do not grind) so they’ll pass through 2 mm screen. Use the NASCO soil grinder only for especially hard clods. Tare a suitable container, weigh, record, and discard the “> 2 mm” portion of sample. Tare a suitable container, weigh and record “< 2 mm” portion. **Do not discard.**
7. The O-horizon samples should be allowed to air dry, but should not be sieved. The O-horizon samples will not be analyzed for MAGIC parameterization, but may be useful in the future for evaluating the nitrogen status of the site. (Note: MAGIC procedures for simulating nitrogen cycling may be updated in the near future and may necessitate analysis of O-horizon samples.) The O-horizon samples should be stored in sealed plastic bags for archiving. The bags should be labeled indicating the site identification code, the sample collection date, and “O-horizon.”
8. Prepare a split for oven-drying the mineral soils after air drying. Zero the balance and record the soil can number in the “Soil Can #” column. Weigh and record the soil can weight including its cover in the “Soil Can Wt (g)” column. Tare the can with its cover and then add 10-15 g of air dried sample. Record the weight under “AD Soil - Can (g).” Place the can and sample with **cover off** in the oven overnight at 105 °C. After oven-drying, replace cover, cool the can and sample in a desiccator for 3 to 5 minutes. Zero the balance, weigh and record the oven dry sample with can under “OD soil + can (g).” **Be sure all columns are filled.** After all data is satisfactory and stored in the Excel spreadsheet, dispose of the OD sample and clean the can for next use. The balance of the dry sieved soil should be packed in sealed plastic bags for archiving. The bags for sample archiving should be labeled indicating the site identification code, the sample collection date, and either “Shallow Sample” or “Deep Sample,” as appropriate. Before disposing of any portion of regulated soil samples or any material that has been in contact with them, they must be sterilized by exposure to elevated temperature. Place soils in appropriate containers such as aluminum turkey roaster pans and heat to at least 121 °C. Once the entire mass has reached that temperature, maintain for at least 2 hours. Packaging and other materials can be placed in autoclave bags before heating to 121 °C. Plastic bags that melt at high temperature might trip the smoke alarm, so must not be placed in oven. These should be securely packaged and stored until incineration can be arranged. Boxes of archived samples from

regulated states should be labeled as such. Spilled soil from regulated states must be swept up and heat-treated as described above. The area of the spill must be sprayed with 70% alcohol solution.

9. Prepare pH, cations, carbon, and archive splits. **Split for pH;** label a paper cup with sample ID. Tare the cup and put in 20.0 g of < 2 mm soil. Deliver samples and cups to the chem lab daily. Do each 20th sample in duplicate and include “dup” on the label. **Split for cations;** label a 20 mL scintillation vial with sample ID and “ICP” for cations so it can be distinguished from a similar carbon split. Fill to about ¾ full (leaving shaking room) with < 2 mm soil. Store in storage room next to lab 31 keeping them separate from carbon splits. **Split for carbon;** label the bottom and side of a 20 mL scintillation vial with sample ID and a “C” for carbon so it can be distinguished from a similar cations split. A label on the cap might be worn off as it turns on the vial rotator. Also place clear tape over the side label to prevent wearing off. Add soil to about 1/3 full, insert two steel tumblers, cap securely, and place the vial on the vial rotator. Some samples will be reduced overnight, others might take 3 or 4 days to reduce to a suitable fine grind. *A mesh size has not yet been determined, so grinding is ended based only on the operator’s observation.* Store the vials in the storage room next to lab 31 keeping them separate from the cations splits. **Split for archive;** In two places, label a 4 oz. specimen container and cap with sample ID. The label must remain legible for up to 30 years. Place the container and cap on a balance and zero the balance. Fill container with < 2 mm soil. Replace the cap, weigh, and record the weight under “Archive Wt (g).” Clean all equipment after each sample, and the entire work area at the end of each day.
10. Archived samples should be stored in plastic tubs with secure lids. The plastic tubs should be labeled to indicate the contents. Storage area housing soils from regulated states must be signed: “Contents: Regulated domestic soil to be used in accordance with USDA APHIS PPQ soil permit and compliance agreement.” Packages containing soils from regulated states must be so labeled. Each sample must be labeled as “Regulated soil under USDA permit.” A SOP describing clean-up of regulated soil spills must be posted in archive and soil preparation areas.

4.5 Soil Sample Analysis

Application of the MAGIC model requires analyses of the following soil properties in both the shallow and deep mineral soil layers. The laboratory performing the analysis needs to be experienced at performing analysis for acid-base chemistry.

- pH (lab measurement)
- Exchangeable bases: calcium, magnesium, potassium, and sodium
- Exchangeable aluminum
- Cation exchange capacity (CEC) or effective CEC for acid soils

Analyses of total nitrogen and total carbon are also recommended.

The following methods are appropriate for analysis of forest soils for assessment of acid-base status and acidification effects in the southern Appalachian Mountains region. All chemical analysis results should be expressed on an oven-dried soil mass basis (70°C for forest floor and 105° C for mineral soils).

4.5.1 Analysis Methods

Currently, the USFS Soils Lab in Grand Rapids, Minnesota will perform the chemical analysis for the soil samples. The following is a summary listing of instrumentation and techniques employed for sample analysis. Equivalent instrumentation and techniques can be substituted, such as those employed by the University of Virginia (see Appendix E). A listing of other possible protocols and methods can be found in Appendix A.

pH (hydrogen ion)

Instrumentation: Mettler Toledo DL53 Titrator with DG111-SC Combination pH Electrode, DT120 Temperature Sensor, Rondo 60 Autosampler, and LabX version 1.0 Software

Technique Summary: Potentiometric measurement in a 1:1 soil to deionized water slurry by mass and in 0.01 M CaCl₂ (Cappo et al., 1987)

Reporting units: standard pH units.

Exchangeable Bases (calcium, magnesium, potassium, and sodium), Exchangeable Aluminum, and Cation Exchange Capacity

Instrumentation: Thermo Elemental Iris Intrepid ICP with Timberline IIL Autosampler and TEVA version 1.5.0 Software

Technique Summary: Extraction by 1.0 N ammonium chloride; analysis by inductively-coupled plasma atomic emission spectrometry (Weaver et al., 1982; SSLMM, 1996)

Reporting units: cmol+ / kg soil

Total Nitrogen and Carbon

Instrumentation: Fisons NA1500 Elemental Analyzer

Technique Summary: combustion (Nelson and Sommers, 1996).

Reporting units: percent dry weight

4.5.2 Data Quality

The quality control and assurance component of soil sampling and analysis should include field duplicates (replicated soil pit in close proximity to the original soil pit), repeated analysis of composite samples (if the soil survey will extend for a period of several weeks or more), and evaluation of data internal consistency (relationships among variables).

Quality control in the field will be achieved through careful site location and close adherence to sampling procedures. Quality control in the laboratory will depend on close adherence to holding time criteria, avoidance of sample contamination, and careful following of instrument operation and calibration procedures.

Approximately 10% of all soil samples should be collected in duplicate, by excavating a second soil pit in close proximity to the first. Results for duplicate analysis should be reported for each analyte as the mean and standard deviation of the absolute differences between duplicate sample pairs. Do not assume that the values are incorrect if results for the second pit differ from the first one. Soil variability on the landscape can be large for any number of reasons.

If an extensive soil sampling survey is to be conducted, soil composite samples (both shallow and deep) should be prepared during the first week of field work, each as a large mix of soil from several ($n = 5$) sites exhibiting a range of expected conditions. This composite sample should be sieved (2 mm), thoroughly homogenized, and air dried. Multiple subsamples should then be drawn from both composites, marked as “deep composite” and “shallow composite”, sealed in zipper-lock style bags, and kept refrigerated. Each week, one of each composite type (shallow and deep) should be dated (date of shipment to laboratory) and submitted to the analytical laboratory for analysis. Time series data illustrating results of repeated results from the same sample will later be used to determine if laboratory procedures were comparable throughout the course of the study, as well as deviations associated with replicate measurements.

4.5 Soil Data Management

The NRIS database will be used to enter the soils protocol document information, site documentation, sample collection record, and analysis record tables. Data entry of the soil information will be accomplished at the Supervisor’s Office of the National Forests in North Carolina. Appendix D provides the field data forms for the soil sampling components of the current project. Instructions for collection of the necessary data have been provided above in the text of this document.

5.0 SAFETY ISSUES

For safety reasons, an emergency contact individual, who is not part of the field crew, should always know where the field crew is going each day, and by what route. This person should be contacted by the field crew immediately upon return from the field each day.

Safety equipment should include, but should not necessarily be limited to, the following:

- Two-way radios and/or cellular telephone
- Extra batteries for GPS and radios
- Rain gear
- Space blanket
- Adequate supply of drinking water
- Sunscreen

- First aid kit

Field personnel should have current first aid and CPR certificates. Field personnel should be instructed to not cross a dangerous stream or excessively steep terrain.

6.0 CITATIONS

- Cappo, K.A., L.J. Blume, G.A. Raab, J.K. Bartz, and J.L. Engels, 1987. Analytical Methods Manual for the Direct/Delayed Response Project Soil Survey. EPA/600/8-87/020, U.S.E.P.A., Washington, DC.
- Cosby, B.J., R.F. Wright, G.M. Hornberger, and J.N. Galloway. 1985a. Modelling the effects of acid deposition: assessment of a lumped parameter model of soil water and streamwater chemistry. *Water Resour. Res.* 21:51-63.
- Cosby, B.J., R.F. Wright, G.M. Hornberger, and J.N. Galloway. 1985b. Modelling the effects of acid deposition: estimation of long-term water quality responses in a small forested catchment. *Water Resour. Res.* 21:1591-1601.
- Gran, G., 1952. Determination of the equivalence point in potentiometric titrations. Part II. *Analyst* 77:661-671.
- Nelson, D.W. and L.E. Sommers. 1996. In D.L. Sparks (ed), *Methods of Soil Analysis, Part 3. Chemical Methods*. Soil Science Society of America Book Series Number 5. American Society of Agronomy, Madison, WI.
- SSLMM (Soil Survey Laboratory Methods Manual), 1996. Soil Survey Investigations Report No.42, Version 3.0. USDA, Natural Resources Conservation Service, National Soil Survey Center, Lincoln, NE.
- Sullivan, T.J. and B.J. Cosby. 2002. Critical loads of sulfur deposition to protect streams within Joyce Kilmer and Shining Rock Wilderness Areas from future acidification. Report prepared for USDA Forest Service. E&S Environmental Chemistry, Inc., Corvallis, OR.
- Sullivan, T.J., B.J. Cosby, J.A. Lawrence, R.L. Dennis, K. Savig, J.R. Webb, A.J. Bulger, M. Scruggs, C. Gordon, J. Ray, E.H. Lee, W.E. Hogsett, H. Wayne, D. Miller, and J.S. Kern. 2003. Assessment of Air Quality and Related Values in Shenandoah National Park. Technical Report NPS/NERCHAL/NRTR-03/090. U.S. Department of the Interior, National Park Service, Northeast Region, Philadelphia, PA.
- Sullivan, T.J., B.J. Cosby, J.R. Webb, K.U. Snyder, A.T. Herlihy, A.J. Bulger, E.H. Gilbert, and D. Moore. 2002. Assessment of the Effects of Acidic Deposition on Aquatic Resources in the Southern Appalachian Mountains. Report prepared for the Southern Appalachian Mountains Initiative (SAMI). E&S Environmental Chemistry, Inc., Corvallis, OR.
- Weaver, R.W., S. Angle, P. Bottomley, and D. Bezdiecek (eds). 1982. In D.L. Sparks (ed), *Methods of Soil Analysis. Part 2. Chemical and Microbiological Properties*. Soil Science Society of America Book Series Number 5. American Society of Agronomy, Madison, WI.

APPENDIX A:

SELECTED LISTING OF PROTOCOLS AND METHODS MANUALS REVIEWED

Blume, L.J., B.A. Shumacher, P.W. Schaffer, K.A. Cappel, M.L. Papp, R.D. Van Remortel, D.S. Coffey, M.G. Johnson, and D.J. Chaloud, 1990. Handbook of Methods for Acid Deposition Studies Laboratory Analyses for Soil Chemistry. EPA/600/4-90/023, U.S.E.P.A., Washington, DC.

Cappel, K.A., L.J. Blume, G.A. Raab, J.K. Bartz, and J.L. Engels, 1987. Analytical Methods Manual for the Direct/Delayed Response Project Soil Survey. EPA/600/8-87/020, U.S.E.P.A., Washington, DC.

Edwards, P.J., and F. Wood, 1993. Field and Laboratory Assurance/Quality Control Protocols and Accomplishments for the Fernow Experimental Forest Watershed Acidification Study. General Technical Report NE-177, USDA Forest Service, Northeastern Forest Experiment Station. Radnor, PA.

Fox, D.G., J.C. Bernabo, and B. Hood, 1987. Guidelines for Measuring the Physical, Chemical, and Biological Condition of Wilderness Ecosystems. USDA Forest Service General Technical Report RM-146, 48 p., Rocky Mountain Forest and Range Experiment Station, Fort Collins, CO.

Morrison, M.L., 1991. Part 1: Quality Assurance Plan for the Long-Term Monitoring Project, in Data User's Guide to the U.S. EPA Long-Term Monitoring Project: Quality Assurance Plan and Data Dictionary. EPA/600/3-91-072, U.S. EPA Environmental Research Laboratory, Corvallis, OR.

NCASI, 1983. Field Study Program Elements to Assess the Sensitivity of soils to Acidic Deposition Induced Alterations in Forest Productivity. Technical Bulletin No. 404, National Council of the Paper Industry for Air and Stream Improvement, Inc. New York, NY.

Shenandoah Watershed Study, Department of Environmental Sciences, University of Virginia, Charlottesville, VA. <http://wsrv.clas.virginia.edu/~swasftp/docs/SOP-021303.pdf>

Turk, J.T., 2001. Field Guide for Surface Water Sample and Data Collection. Air Program, USDA Forest Service.

U.S.E.P.A., 1989. Handbook of Methods for Acid Deposition Studies: Field Operations Manual for Surface Water Chemistry. EPA/600/4-89/020, U.S.E.P.A., Washington, DC.

U.S.E.P.A., 1987. Handbook of Methods for Acid Deposition Studies: Laboratory Analyses for Surface Water Chemistry. EPA/600/4-87/026, U.S.E.P.A., Washington, DC.

USFS/USGS Water & Soils Lab, Rocky Mountain Research Station, Fort Collins, CO. <http://www.fs.fed.us/rm/waterlab/Labprotocols.htm>

APPENDIX B:

FOREST SERVICE DATA COLLECTION FORMS AND INSTRUCTIONS

- (1) Surface Water Chemistry Long-Term Monitoring Record**
- (2) Chain of Custody Form**

Surface Water Chemistry Long-Term Monitoring Record

Site Information

revised 04/08/2004

Stream ID		Stream Name	
Latitude	Longitude	Location Description (e.g., west side of lake near weir)	
Hydrologic Unit Code		National Hydrography Data (NHD) Reach Code	
National Forest		Wilderness	
Ranger District		Other Administrative Name (e.g. Research Natural Area, Experimental Forest)	
Elevation (m)		Stream Order (N/A for lakes)	Lithology
Catchment Slope (%)	Catchment Aspect (e.g., N, SW, NE)		Catchment Size (ha)
% of Catchment above the Sample Site:	Hardwoods___ Conifer ___	Exposed Bedrock Or soil ___	Meadows/ Shrubs ___ Other ___

Sample Information

Technician Responsible: Last Name		First Name		Phone No: Area code _____ Number _____ - _____
Date (mm/dd/yyyy)	Time (hh24mm)	Sample Measurement Location (Please use Type Table)	Sample Depth Zone (Please use Type Table)	
GPS Latitude (decimal degrees) (x.xxxx)		GPS Longitude (decimal degrees) (x.xxxx)		Stream Stage (please circle) Rising, Falling, Steady, Peak, Baseflow
Usual Collection Point? Y___ N___ If no, why?			Observed Water Level (please circle) High, Medium, Low	Measurement Sampling Depth (m)
Sample ID (ID sent to lab, bar code) (Please attach chain of custody)			Sampling Method (please circle) Grab, Composite, Shallow, Pole, Auto, Point	Type of Sample (please circle) Regular, Duplicate, Triplicate, Blank, Split, Other
Did sample collection deviate from protocol? Y___ N___ If yes, describe				
Field Notes and Observations (Vegetation: significant differences from last site visit, clarity, color, fish, photos taken, etc.) (Please attach a separate sheet if needed.)				Percent snow or ice cover in the catchment above the stream

Field Measurements

pH (s.u.)	pH Equipment (make/model #)	Conductivity @ 25°C (uS/cm)	Conductivity Equipment (model #)	Water Temperature (°C)
Wind Speed (m/s) (see Wind speed scale)		Wind Direction (from N, NW, etc.)		Precipitation during collection? (yes or no)
Cloud Cover (nearest 10%)		Barometric Pressure (mmHG)		Air Temperature (°C)

Wind Speed Scale

Mean Speed (m/s)	Description		Land Specifications Use at streams		Water Specifications Use at lakes
0	Calm		No leaf movement		Water like glass
0.8	Light air		Leaves quiver		Water ripples
2.4	Light breeze		Leaves rustle		Small wavelets: crests have
4.3	Gentle breeze		Leaves and small twigs in constant motion		Large wavelets: crests begin to break
6.7	Moderate breeze		Small braches move		Small waves: frequently white caps
9.3	Fresh breeze		Small leafed trees sway		Moderate waves: Many white caps
12.3	Strong breeze		Large branches move		Large waves: spray off white caps
15.5	Near gale		Whole trees sway		White foam blown from breaking waves
> 18.9	Gale or stronger		Twigs break of trees		Very high waves

Sample Measurement Location Type Table

Type	Description
BANK	Bank – Stream waters edge
DEEP	Over deepest spot of the Stream flow. Pools typically occur where the river bends or meanders
POOL	Stream Pool – An area of the stream with greater than average depth and slower than average flow. Pools typically occur where the river bends or meanders.
RIFL	Stream Riffle - A raised area of the active channel that results in an increase in flow velocity. Riffle areas are typically preceded by pools and represent the fastest current in a given river or stream.
UNKN	Unknown

Sample Depth Zone Type Table

Type	Description
WTRS	Stream Water surface
WUBT	Stream Water bottom
UNKN	Unknown

Instructions for Completing the Form: Surface Water Chemistry Long-Term Monitoring Record

The following Site Information section should be completed in the office prior to departing for the field as many of the entries require reference materials.

1. Enter the Stream ID. To determine a new identifier you will use the decimal degree Longitude and Latitude. It will consist of 13 digits where the first 7 digits are the decimal degree longitude and the last 6 digits will be the decimal degree latitude. All values will begin with 0 as the first character
2. Find the common Stream Name on the 1:24,000 topographic map.
3. Select Latitude and Longitude for the sampling point from a map. Enter in decimal degrees (xxx.xxxx).
4. The Hydrologic Unit Code (HUC) is the 11 digit code determined using ArcMap for the appropriate 5th level HUC
5. Find the National Hydrography Data (NHD) Reach Code at a 1:24,000 scales. Eventually the National Hydrography Data web site <http://nhd.usgs.gov/> will provide the data sets, and in the NRIS spatial database.
6. Find the National Forest, Ranger District, Wilderness and Other Administrative Name, if one exists, on the appropriate Forest Recreation map.
7. Calculate the average Elevation (meter) of the catchment using spatial analyst
8. The Stream Order is determined as follows: Expressed numerically the smallest permanent streams are called "first order" or #1 streams. Two first order streams join to form a larger stream are second order streams or #2 streams; two second order streams join to form a third order stream or #3 streams, and so on. Smaller streams entering a higher-ordered stream do not change its order number.
9. Find the Lithology by using the identify tool in ArcMap.
10. Calculate the average Catchment Slope by using Spatial Analyst and the Zonal Statistic analysis tool.
11. Calculate Catchment Size, that is, the area that forms the watershed for the stream using XTool and ArcMap.
12. Use an aerial photo, if available, to estimate the percentage of surface cover that is Hardwoods, Conifer, Exposed Bedrock, Meadows/Shrubs and Other.

The following Sample Information should be collected in the field.

1. Enter Technician Name and Phone Number. Self explanatory (SE)
2. Date and Time. SE.
3. Enter Sample Measurement Location 4-letter code from attached table.
4. Enter Sample Depth Zone 4-letter code from attached table.
5. Enter Latitude and Longitude (decimal degrees) for the sampling point from a GPS, if available.
6. Check the Usual Collection Point. If no, briefly mention why.
7. Circle Observed Water Level.

8. Enter Measurement Sampling Depth to the hundredth of a meter.
9. Enter Sample ID. For example Sample ID 0020302160001-1M would be identified as follows: Julian day (002), Year (03), Region (08), Forest Number (XX; Cherokee = 04, Francis Marion and Sumter = 12, and National Forests in North Carolina = 11), Unique number derived from the field unit (0001). See Julian day calendar appropriated Julian day.
10. Circle Sampling Method. A Grab sample is taken a selected location, depth and time usually near shore; a Composite sample is made by mixing several discreet samples into one; Shallow samples are made by creating a small dam to create enough depth to get a bottle submerged; a Point (depth) sample is taken at a single depth usually with a special bottle such as a Van Dorn; a Pole sample is taken by attaching a bottle to pole but is otherwise similar to a grab sample; an Auto sample is collected by an autosampler.
11. Circle Type of Sample. A Duplicate sample is collected at some short distance from the regular sample to assess short-range spatial variability; a Triplicate sample has the same objective as a duplicate only with yet a third sample collected at some other point; a Blank is a prepared sample of distilled or deionized water; a Split is a regular sample split into two bottles to evaluate sample homogeneity.
12. Did the Sample Collection Deviate from this Protocol document? How?
13. Enter Field Notes and Observations. SE
14. Estimate the Snow Cover Percentage, if any, in the catchment.

The following Field Measurements to be collected primarily while in the field.

1. Find Water Temperature to tenth of a degree centigrade.
2. Enter the water pH by using a probe in the water body to the nearest tenth of a standard unit.
3. What pH Equipment make and model was used, if any?
4. Enter the Specific Conductance by using a probe into the water body to three significant figures of a uS/cm.
5. What Specific Conductance Equipment make and model was used?

The following Weather Conditions to be entered while in the field.

1. Enter the estimated Wind Speed to the nearest whole m/s using the attached table.
2. Estimate the nearest cardinal Wind Direction from which the wind is blowing using a compass.
3. Was it Precipitating During the Data Collection?
4. Estimate the Cloud Cover to the nearest tenth of the sky dome.
5. Enter the Barometric Pressure (not sea level pressure or altimeter setting) to the nearest hundredth of a mm of Hg.
6. Enter the Air Temperature to the nearest of a whole centigrade degree.



Chain of Custody Form

Revised:4/2/2004

Forest/Wilderness/Park/Other (Circle one)				Original Chain of Custody to the attention of:				Phone #	
Unit From:								Fax #	
Address:				Shipped to by (UPS/Fed Ex/USPO)					
City, State, Zip:				Shipping #				Page ____ of ____	

Date Sampled	Time Sampled	Sample ID	Location	Sample Collected by	Type (regular, blank, dup.)	Filtered (Y/N)	Preserved (Y/N/ Type)	Analyses Requested	LabID

Comments:

Received/Relinquished by:			
<i>Print Name</i>	<i>Signature</i>	<i>Date & Time Received</i>	<i>Date & Time Relinquished</i>
Received at Laboratory by:			
<i>Print Name</i>	<i>Signature</i>	<i>Date</i>	<i>Time</i>
Processed at Laboratory by:			
<i>Print Name</i>	<i>Signature</i>	<i>Date</i>	<i>Time</i>

Please send this form to the contracted laboratory and make a copy for yourself.

Instruction for Completing the Chain Of Custody Form

Forest/Wilderness/Park/Other (Circle one): Circle one of these options and write the name of the Forest/Wilderness/Park or other in the space below.

Unit From: This could be a separate unit within the Forest, Wilderness, Park or Other (ie. Subcontractor)

Address: Address of the Forest, Wilderness, Park or Other (ie. Subcontractor)

City, State, Zip: City, state, zip code of the Forest, Wilderness, Park or Other (ie. Subcontractor)

Original Chain of Custody to the attention of: Name, address, email, etc. of the person the data results and original Chain of Custody form will be sent to.

Phone #: Phone number of the person the data results and original Chain of Custody form will be sent to.

Fax #: Fax number of the person the data results and original Chain of Custody form will be sent to.

Shipped to by (UPS/Fed Ex/USPO): Which carrier you used. (**Remember to consider that on weekends and government holidays there is not anyone to receive samples in the laboratory**)

Shipping #: Tracking number assigned to the shipment by the carrier.

Page ____ of ____: Page number(s) of Chain of Custody forms sent.

Date Sampled: Date sample was taken.

Time Sampled: Time sample was taken.

Sample ID: Unique identification number assigned to sample to for tracking purposes. (ie. Bar code or unique identifier used to identify the sample for connectivity of field analysis with the laboratory analysis)

Location: Location description of sample site (ie. Lake name, stream name.)

Sample Collected by: Person collecting the sample.

Type (regular, blank, dup): Type of sample collected such as regular water, field blank, duplicate, etc.)

Filtered (Y/N): Was this sample filtered in the field?

Preserved (Y/N): Was this sample preserved in the field and with what kind of preservative (ie. H₂SO₄)

Analyses Requested: Instructions for laboratory requesting what type of analysis is to be performed (ie. ANC, pH, Conductivity, Major Cations, Anions, Totals, etc.)

LabID: A unique identifier created by the laboratory to track the samples (if they are not using the Sample ID).

Comments: Any extra remarks or instructions are placed in this space.

Received/Relinquished by:

Print Name: Printed name of sampler relinquishing the samples to another person for shipment to the laboratory or directly to the laboratory.
Signature: **Sampler's signature relinquishing the samples to another person for shipment to the laboratory or directly to the laboratory.**

Date & Time Received: Date and time samples were received from the sampler.

Date & Time Relinquished: Date and time relinquished by the sampler or by person shipping samples to the laboratory.

Received at Laboratory by:

Print Name: Printed name of laboratory personnel receiving the samples.
Signature: Signature of the laboratory personnel receiving the samples.
Date: **Date the samples were received by the laboratory.**

Time: Time the samples were received by the laboratory.

Processed at Laboratory by:

Print Name: Printed name of laboratory personnel processing the samples.
Signature: Signature of the laboratory personnel processing the samples.
Date: **Date the samples were processed by the laboratory.**

Time: Time the samples were processed by the laboratory.

APPENDIX C:

A Summary Listing of Instrumentation and Techniques Employed by the University of Virginia for Water Analysis

The following is a summary listing of instrumentation and techniques employed by the University of Virginia (<http://www.swas.evsc.virginia.edu/methods>). The following is included because it serves as an alternative acceptable laboratory that other people interested in this document can compare against to obtain adequate data for the MAGIC model.

pH (hydrogen ion)

Instrumentation: Beckman Psi 21 pH meter (Part No. 123114) Corning Calomel Combination pH Electrode (Cat. Nos. 476530)

Technique Summary: Potentiometric measurement with open-system samples. Within-aliquot stability (<0.01 units/min.) and sequential-aliquot agreement (<0.03 units difference) obtained for all readings. Lab measurement is recommended due to difficulties associated with field measurement. (USEPA, 1987)

Reporting units: standard pH units

Acid-Neutralizing Capacity

Instrumentation: Beckman Psi 21 pH meter (Part No. 123114) Corning Calomel Combination pH Electrode (Cat. Nos. 476530) Technique

Technique Summary: Two-point Gran titration with 100 ml sample volumes and 0.005 N HCl titrant. Titration endpoints are approx. 4.5 and 4.2. Within-aliquot stability (<0.01 units/min.) should be obtained for endpoint determinations. (Gran, 1952)

Reporting units: $\mu\text{eq/L}$

Conductivity

Instrumentation: YSI Model 31 Conductivity Bridge; Beckman CEL-GO1 cell

Technique Summary: Standard conductivity bridge and cell, values corrected to 25 degrees C (USEPA, 1987).

Reporting units: $\mu\text{S/cm}$

Sulfate, Chloride, Nitrate

Instrumentation: Dionex 4000i Ion Chromatograph; HPIC AS4A Separator Column; HPIC AG4A Pre-Column; AMMS Anion Micro-Membrane Suppressor

Technique Summary: Simultaneous determination by ion chromatography. Injection volume: 200 μL . Eluent: 2.2 ml 3.5-4.5 mM Sodium Carbonate/minute. Regenerant: 3-4 ml .035 N Sulfuric Acid/minute. (USEPA, 1987)

Reporting units: $\mu\text{eq/L}$

Calcium, Magnesium, Potassium, Sodium

Instrumentation: Thermo Jarrell Ash AA/AE Spectrophotometer Model Smith-Hieftje 22

Technique Summary: Flame atomic absorption spectrophotometry. Li/La added to aliquot (Galloway et al., 1982).

Reporting units: $\mu\text{eq/L}$

Fluoride

Instrumentation: Orion Fluoride Combination Electrode Model 96900

Technique Summary: Determination by ion-selective electrode (USEPA, 1987).

Reporting units: $\mu\text{eq/L}$

Aluminum, total monomeric and inorganic monomeric

Instrumentation: Technicon Autoanalyzer II

Technique Summary: Colorimetric detection with open-system samples by pyrocatechol violet technique. Fractionation with ion-exchange resin. (McAvoy et al.,1992)

Reporting units: $\mu\text{g/L}$

Dissolved organic carbon

Instrumentation: Dohrmann Carbon Analyzer

Technique Summary: Persulfate/UV oxidation with infrared detection (USEPA, 1987).

Reporting units: mg/L

APPENDIX D:

Field Data Forms for the Soil Sampling Components of the Assessment Project

SOILS FIELD DATA FORM

(Complete one form for each the O-horizon, shallow and deep samples)

Sample ID (<i>place on bags</i>):	Date (<i>mm/dd/yy</i>): _____ Time (<i>hh24mm</i>): _____	National Forest (<i>circle one</i>): Pisgah, Nantahala, Cherokee, or Sumter
Hydrologic Unit Code:		Ranger District:
GPS Location (<i>decimal degrees</i>): Longitude: _____ Latitude: _____		Wilderness or Other Administrative Name:
Site ID (based upon latitude and longitude):		USGS 7.5 topo map:
Elevation (<i>m</i>):		Sketch Profile (describe colors using Munsell chart and measure depth of each horizon):
Tag number and description of tag tree:		
Soils Map Unit:		
General Soil Description (Attach map unit description to this sheet)		
Vegetation Type (<i>circle one</i>): hardwood, conifer, open field, hardwood-conifer, conifer-hardwood, or brush		
Local Disturbance:		Photograph number(s): _____
Deviations from Sampling Site Protocols (especially depth):		
Estimated Percent Coarse Fragments: Indicate Range (<i>circle</i>)	<u>Shallow Sample</u> < 15 15 to <35 35 to <60 60 to < 90 ≥ 90	<u>Deep Sample</u> < 15 15 to <35 35 to <60 60 to < 90 ≥ 90
Describe Coarse Fragments (i.e., size, shape, aggregation):		
Narrative access and site description (Any problems finding or getting to the site?):		
Soils layer (<i>circle</i>): O-horizon, shallow, deep	Size (diameter) of O-horizon sample collected (cm) _____	
Type of Sample (<i>circle</i>): Regular, Duplicate	Depth of mineral soil sampling pit (cm) _____	
Technician Responsible: Last Name	First Name	Phone Number: Area Code _____ Number _____ - _____

APPENDIX E:

A Summary Listing of Instrumentation and Techniques Employed by the University of Virginia for Soils Analysis

pH (hydrogen ion)

Instrumentation: Beckman Psi 21 pH meter (Part No. 123114) Corning Calomel Combination pH Electrode (Cat. Nos. 476530)

Technique Summary: Potentiometric measurement in a 1:1 soil to deionized water slurry by mass and in 0.01 M CaCl₂ (Cappo et al., 1987)

Reporting units: standard pH units.

Exchangeable Bases (calcium, magnesium, potassium, and sodium)

Instrumentation: Thermo Jarrell Ash AA/AE Spectrophotometer Model Smith-Hieftje 22

Technique Summary: Extraction by 1.0 N ammonium chloride; analysis by flame atomic absorption spectrophotometry (SSLMM, 1996).

Reporting units: cmol+ / kg soil

Exchangeable Aluminum

Instrumentation: Thermo Jarrell Ash AA/AE Spectrophotometer Model Smith-Hieftje 22

Technique Summary: Extraction by 1.0 N potassium chloride, analysis by flame atomic absorption spectrophotometry (Weaver et al., 1982).

Reporting units: cmol+ / kg soil

Cation Exchange Capacity

Instrumentation: Thermo Jarrell Ash AA/AE Spectrophotometer Model Smith-Hieftje 22

Technique Summary: Extraction by 1.0 N ammonium chloride, analysis by flame atomic absorption spectrophotometry (SSLMM, 1996).

Reporting units: cmol+ / kg soil

Total Nitrogen and Carbon

Instrumentation: Fisons NA1500 Elemental Analyzer

Technique Summary: combustion (Nelson and Sommers, 1996).

Reporting units: percent dry weight